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Stable Solutions of Mixtures of Naphthols
and Stabilized Diazo CompoundsJulian J. Leavitt, Plainfield, New Jersey, U.S.A.,
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EXAMINER'S
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1 This invention relates to stable solutions comprising a mixture of a stabilized diazo compound and a naphthol. More specifically, it relates to stabilized solutions of beta-hydroxynaphthoic arylides and p-aminodiphenylamines, diazotized and coupled to secondary aliphatic amino acids such as N-methylglycine and N-methyltaurine.

The azoic dyestuffs comprise a class of azo dyestuffs which are used widely commercially. They are formed by coupling of unsulfonated diazonium compounds with unsulfonated naphthols. Such coupling usually must be carried out in situ on the cloth because of the insolubility of the final dyestuffs. This coupling on the cloth can be carried out in a number of ways. One such procedure is successive immersion of the cloth in solutions of the diazo compound and of the naphthol. Another method is to impregnate the cloth with the naphthol and to use the other component in the form of a print paste to produce a design on the cloth. The most common methods of applying these dyestuffs utilize the stability of certain derivatives of the diazotized amines such as the zinc chloride double salts and the diazoamino compounds prepared by coupling the diazo compound with an amino acid. The stabilized diazo compounds of the latter type can be mixed with the naphthols in alkaline solutions. Such solutions, when applied to the cloth and followed by subsequent acid treatment, produce a dyestuff in situ. This acid treatment is generally known as acid aging and operates through the decomposition of the diazoamino compound to regenerate the diazo compound which in turn immediately couples with the naphthol.

Such mixtures of stabilized diazo compounds and naphthols are usually sold as powders. These powders have the disadvantage that the user must make sure of getting all in solution in order to achieve a standard strength dyeing. This problem can sometimes be time-consuming and always forms an extra step for the user. Recently, these mixtures have been sold in the form of concentrated solutions which have the advantage of being usable by the dyer without worrying about effecting solution. They can be diluted to form dyebaths or mixed with other ingredients to form print pastes. In either case a homogeneous mixture is obtained.

Certain of these dyestuffs are not usable in the form of solutions at present because the solutions are unstable to storage. They decompose slowly,

2 even in the presence of excess alkali, to evolve nitrogen and to produce precipitates, probably of the dyestuffs. This decomposition gives a lowering in the strength of the dyestuff on standing and makes it impossible for the dyer to produce uniform dyeings over periods of time. Since the dyestuff manufacturer cannot control the interval between the manufacture and the use of his product, it is essential that the solutions of azoic dyestuffs be stable for long periods of time.

Among the dyestuffs which give trouble are those formed by mixing stabilized diazos derived from p-aminodiphenylamines with arylides of 3-hydroxy-2-naphthoic acid, especially Naphthol AS itself which is the anilide of 3-hydroxy-2-naphthoic acid. Aminodiphenylamines of particular interest are 4-aminodiphenylamine, 4-amino-4'-methoxydiphenylamine and 4-amino-3-methoxydiphenylamine. In our invention, stable solutions of these dyestuffs may be prepared when up to 35% of the diazo compound stabilized by methylglycine—(used in the form of its alkali metal salts)—is mixed with at least a stoichiometric quantity of the Naphthol; at least a stoichiometric quantity of caustic; at least 15% of an organic solvent of the lower alkyl monoethers of glycol; and at least 15% of a tertiary amine of the formula



30 in which R_1 represents a hydroxyalkyl radical and R_2 and R_3 are lower alkyl or hydroxy alkyl radicals. In this description and in the claims the term "lower alkyl radical" will be used in the usual sense to denote hydrocarbon chains of no more than six carbon atoms. I prefer to have no more than 20% of the stabilized diazo present by weight in the above composition. Such solutions are stable for long periods and can be used directly in dyebaths and in formulating print pastes.

Coupling components of special importance because they give blue dyes of outstanding fastness with these bases are Naphthol AS, which is the anilide, and Naphthol AS-D, which is the o-toluidide of 3-hydroxy-2-naphthoic acid. The usage of the naphthol depends primarily on the usage of the stabilized diazo, since it must be present at least in stoichiometrically equivalent quantity.

The bases which can be added to form the stable

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solutions of our invention are preferably potassium hydroxide or sodium hydroxide. However, any water-soluble, moderately strong base can be used. Examples of other bases which may be used are quaternary ammonium hydroxides. In order to keep the naphthol in solution, particularly on dilution with water, the usage of caustic must be at least stoichiometrically equivalent to the naphthol usage and excesses of the order of 50-100% of this minimum are greatly to be preferred.

The organic solvent which is added to help stabilize the solution can be any one of the hydrophilic solvents of the class consisting of the lower alkyl monoethers of glycol (known as the cellosolves) such as the mono-methyl, mono-ethyl, mono-propyl, mono-butyl glycols and the like. The mono-ethyl ether of glycol, usually called "Cellosolve", is the preferred solvent. The solvent usage must be at least 15% of the total weight and is preferably of the order of magnitude of about 30%.

The amine which is added to stabilize the solution may be any tertiary amine in which at least one of the three groups attached to the nitrogen is a hydroxy alkyl group such as $-C_2H_4OH$, and the other substituents on the amino nitrogen are either lower hydroxy alkyl or lower alkyl groups. The preferred amine of this class is triethanolamine. The minimum usage of amine is 15% of the total weight and should preferably be of the order of magnitude of about 30%. Preferably, also, the amount of amine used should be somewhat near that of the solvent used.

The method of preparing these solutions is not important to the operability of the invention. The ingredients can be mixed in any order desired. The mixture can be effected most conveniently if the order of the addition is naphthol, solvent, caustic, diazoamino compound, and lastly water. The amount of water added depends on the amounts of the other ingredients, sufficient being added to make up the predetermined composition.

I do not understand why it is necessary to have both an organic solvent and a tertiary amine of the type described above in order to achieve stabilized solutions, and I do not wish to be limited to any theory thereon. It is necessary, however, that both these components be used as the use of one or the other alone does not produce a stable solution.

My invention can be illustrated by the following examples in which parts are by weight unless otherwise indicated.

Example 1

A mixture was prepared composed of:

| | |
|----------------------------------------------------------------------------------------------------|--|
| 1.34 parts of 3-hydroxy-2-naphthanilide | |
| 7.52 parts of 2-ethoxyethanol | |
| 7.54 parts of 80% triethanolamine | |
| 2.32 parts of 5.15 molar potassium hydroxide | |
| 2.61 parts of the sodium salt of N-(4-(p-methoxy-anilino)-phenylazo)-N-methylglycine (59.3% assay) | |
| 3.47 parts of water | |
| 25.00 parts total | |

The resultant clear brown solution was stable after three weeks.

A similar solution prepared using an additional 7.54 parts of water and no triethanolamine started to evolve gas after three days; after three weeks an appreciable amount had evolved and a sediment had formed.

When the 2-ethoxy-ethanol was replaced by an equal weight of water, the solution showed considerable gassing and precipitation of solid when stored for three weeks.

Example 2

A mixture was made composed of:

| | |
|-----------------------------------------------------------------------------------------------------|--|
| 64.7 parts of 3-hydroxy-2-naphthanilide | |
| 200.0 parts of 2-ethoxyethanol | |
| 200.6 parts of 80% triethanolamine | |
| 115.2 parts of 5.15 molar potassium hydroxide | |
| 122.3 parts of the sodium salt of N-(4-(p-methoxy-anilino)-phenylazo)-N-methylglycine (56.5% assay) | |
| 297.2 parts of water | |
| 1000.0 parts total | |

Samples of the mixture were stored for six months at both 40°C. and at room temperature. The solutions after this time showed only faint traces of sediment and dye tested at full strength versus freshly prepared mixtures.

Example 3

A mixture was prepared composed of:

| | |
|----------------------------------------------------------------------------------------|--|
| 6.47 parts of 3-hydroxy-2-naphthanilide | |
| 15.00 parts of 2-ethoxyethanol | |
| 15.00 parts of 80% triethanolamine | |
| 11.78 parts of 5.15 molar potassium hydroxide | |
| 8.14 parts of the sodium salt of N-(4-anilinophenyl-azo)-N-methylglycine (85.8% assay) | |
| 43.61 parts of water | |
| 100.00 parts total | |

The mixture after being allowed to stand for six weeks showed only a trace of evolution of gas and dye tested at equal strength against freshly prepared solutions.

A similar mixture in which the triethanolamine was replaced by an equal amount of water showed evolution of gas and precipitation of solids within two days.

Example 4

A mixture of:

| | |
|-----------------------------------------------------------------------------------|--|
| 140 parts of the sodium salt of N-4-(p-methoxy-anilino)-phenylazo-N-methylglycine | |
| 131.5 parts of 3-hydroxy-2-naphthanilide | |
| 150 parts of 2-ethoxyethanol | |
| 150 parts 80% solution of triethanolamine | |
| 56.1 parts of potassium hydroxide | |
| 72.4 parts of water | |
| 700.00 parts total | |

was prepared. The mixture was as stable as that prepared in Example 2.

Example 5

A mixture like that in Example 2 was prepared with tetraethyl ammonium hydroxide substituted for the potassium hydroxide. This mixture was equally stable.

Example 6

A mixture was prepared composed of:

| | |
|--------------------------------------------------------------------------------------------------|--|
| 54 parts of 3-hydroxy-2-naphthanilide | |
| 200 parts of 2-ethoxyethanol | |
| 200 parts of methyl diethanolamine | |
| 115 parts of 5.15 molar potassium hydroxide | |
| 122 parts of the sodium salt of N-(4-(p-methoxy-anilino)phenylazo)-N-methylglycine (56.5% assay) | |
| 309 parts of water | |
| 1000 parts total | |

This mixture was also found to be stable. Similar results are obtained when 200 parts of diethylaminoethanol was used in place of the amine used above.

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Example 7

A mixture like that of Example 3 was prepared substituting the beta-oxynaphthoic o-toluidide for the corresponding anilide. The resultant mixture was found to be stable and to keep its dye strength for a period of many weeks.

Example 8

A mixture like that of Example 1 was prepared substituting an equivalent amount of the sodium salt of N-(4-anilinoanisylazo)-N-methylglycine for the sodium salt of N-(4-(p-methoxyanilino)-phenylazo)-N-methylglycine. The resulting mixture was stable.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A stable aqueous solution comprising no more than 20% by weight of an alkali metal salt selected from the group consisting of alkali metal salts of N-(4-anilinophenylazo)-N-methylglycine, alkali metal salts of N-(4-(p-methoxyanilino)-phenylazo)-N-methylglycine, and alkali metal salts of N-(4-anilinoanisylazo)-N-methylglycine, at least a stoichiometric amount of an arylide of 3-hydroxy-2-naphthoic acid; at least 15% by weight of a lower alkyl monoether of ethylene glycol, at least 15% by weight of an amine having the formula:



in which R_1 is a lower hydroxyalkyl radical and R_2 and R_3 are selected from the group consisting of lower alkyl radicals and lower hydroxyalkyl radicals; and a quantity of water soluble base at least stoichiometrically equal to the amount of arylide present.

2. The composition according to claim 1 in which the lower alkyl ether of ethylene glycol is the ethyl ether.

3. The composition according to claim 1 in which the tertiary amine is triethanolamine.

4. The composition according to claim 2 in which

the tertiary amine is triethanolamine.

5. The composition according to claim 4 in which the water soluble base is sodium hydroxide.

6. A stable aqueous solution comprising no more than 20% by weight of the sodium salt of N-(4-(p-methoxyanilino)-phenylazo)-N-methylglycine, at least a stoichiometric amount of 3-hydroxy-2-naphthanilide, at least 15% by weight of 2-ethoxyethanol, at least 15% by weight of triethanolamine and an amount of potassium hydroxide at least stoichiometrically equal to the amount of 3-hydroxy-2-naphthanilide present.

7. A stable aqueous solution comprising no more than 20% by weight of the sodium salt of N-(4-(p-methoxyanilino)-phenylazo)-N-methylglycine, at least a stoichiometric amount of 3-hydroxy-2-naphthanilide, at least 15% by weight of 2-ethoxyethanol, at least 15% by weight of methyl diethanolamine and a quantity of potassium hydroxide at least stoichiometrically equal to the amount of 3-hydroxy-2-naphthanilide present.

8. A stable aqueous solution comprising no more than 20% by weight of the sodium salt of N-(4-anilinoanisylazo)-N-methylglycine, at least a stoichiometric amount of 3-hydroxy-2-naphthanilide, at least 15% by weight of 2-ethoxyethanol, at least 15% by weight of triethanolamine and an amount of potassium hydroxide at least stoichiometrically equal to the amount of 3-hydroxy-2-naphthanilide present.

9. A stable aqueous solution comprising no more than 20% by weight of the sodium salt of N-(4-anilinophenylazo)-N-methylglycine, at least a stoichiometric amount of 3-hydroxy-2-naphthanilide, at least 15% by weight of 2-ethoxyethanol, at least 15% by weight of triethanolamine and an amount of potassium hydroxide at least stoichiometrically equal to the amount of 3-hydroxy-2-naphthanilide present.

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